SOLUTIONS OF THE DIRAC-FOCK EQUATIONS AND THE ENERGY OF THE ELECTRON-POSITRON FIELD

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Abstract. We consider atoms with closed shells, i.e., the electron number N is $2,\ 8,\ 10, ...$, and weak electron-electron interaction. Then there exists a unique solution γ of the Dirac-Fock equations $[D^{(\gamma)}_{g,\alpha}, \gamma] = 0$ with the additional property that γ is the orthogonal projector onto the first N positive eigenvalues of the Dirac-Fock operator $D^{(\gamma)}_{g,\alpha}$. Moreover, γ minimizes the energy of the relativistic electron-positron field in Hartree-Fock approximation, if the splitting of $\mathfrak{H} := L^2(\mathbb{R}^3) \otimes \mathbb{C}^4$ into electron and positron subspace, is chosen self-consistently, i.e., the projection onto the electron-subspace is given by the positive spectral projection of $D^{(\gamma)}_{g,\alpha}$. For fixed electron-nucleus coupling constant $g := \alpha Z$ we give quantitative estimates on the maximal value of the fine structure constant α for which the existence can be guaranteed.

1. Introduction

Heavy atoms should be described by relativistic quantum electrodynamics. Following this idea, Bach et al. [1] showed that the energy of the relativistic electron-positron field in Hartree-Fock approximation interacting with the second quantized Coulomb field of a nucleus is non-negative (if the quantization is chosen with respect to external field) and that the vacuum is a minimizer. Moreover, they showed that the quantization with respect to the external field is optimal in the sense that any other quantization yields a lower ground state energy.

Barbaroux et al. [3] addressed the existence of atoms in the above model, i.e., they prescribed the charge of the electron-positron field and showed that the corresponding functional has a minimizer which fulfills the no-pair Dirac-Fock equations.

The existence of solutions of the Dirac-Fock equations was shown by Esteban and Séré [6] and Paturel [11]. Moreover, Esteban and Séré [5] considered the nonrelativistic limit of the Dirac-Fock equations. They showed that certain solutions of the Dirac-Fock equations converge to the energy minimizing solutions of the nonrelativistic Hartree-Fock equations when the speed of light tends to infinity. This allows them to define the notion of ground state solutions and ground state energy of the Dirac-Fock equations.

In the spirit of Mittleman [9] the physical energy should be obtained by maximizing the ground state energy (as defined, e.g., in [3]) over all allowed one-particle electron subspaces. One might conjecture that a corresponding ground state is a solution of the Dirac-Fock equations. Moreover, such a solution of the Dirac-Fock equations should minimize the energy among all solutions of the Dirac-Fock equations. We call this for brevity the "Mittleman conjecture".

The validity of Mittleman's conjecture was already addressed by Barbaroux et al. [2]. They confirmed it when the atomic shells are closed and the electron-electron interaction is weak (large velocity of light). In the open shell case it was only proven by Barbaroux et al. [4] in the case of hydrogen. All other cases are unknown.

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A stronger conjecture – for brevity called in the paper BES conjecture – would be: the maximin pair (maximizing Λ and minimizing γ) is a projector onto the first N eigenfunctions of the self-consistent Dirac-Fock operator and that Λ is the spectral projector onto the negative spectral subspace of this operator. Barbaroux et al. [2] showed that this conjecture is incorrect in the open shell case in the non-relativistic limit. (For $N = 1$ this result can be extended beyond the limiting case (Barbaroux et al. [4]).) However, they confirm their conjecture for closed shell atoms in the non-relativistic limit.

In this paper – following Barbaroux et al. [2] – we also consider the limit of weak electron-electron interaction. Similarly to Barbaroux et al.[2, Proposition 8] and Esteban and Séré [5, Theorem 5] we prove the existence of a unique solution of the Dirac-Fock equations with the property that the eigenvalues of the solutions are the lowest eigenvalues of the corresponding self-consistent Dirac-Fock operator and that the next eigenvalue is strictly bigger. Again similarly to Barbaroux et al. and Esteban and Séré [5, Theorem 6] this allows us to prove that this solution is the minimizer of the Dirac-Fock energy on the set of all solutions of the Dirac-Fock equations with non-negative eigenvalues. However, we can prove that this solution minimizes the Dirac-Fock energy even on the set of *all* charge density matrices (see the corresponding result of Barbaroux et al. [2, Proposition 8, Equation (15)]) if the quantization is chosen with respect to this solution. We emphasize that we do not only admit positrons in the charge density matrices γ; in fact we can drop the assumption that off-diagonal elements of γ vanish, a requirement inherent in Barbaroux et al. (Corollary 6). Eventually, we show that the minimizer is uniquely determined and spherically symmetric in a certain sense. It has eigenfunctions (orbitals) that respect the Aufbau principle.

The essential novelty of our result is twofold: First, our proof is sufficiently direct and simple allowing for explicit estimates. This enables us to show not only existence results (Esteban and Séré [6] and Paturel [11]) but also to prove important properties of the solutions. In addition we obtain these properties not only in the non-relativistic limit (Barbaroux et al. [2]) but we get explicit estimates on the allowed coupling constants for which these results hold. Second, we can show the minimization property among *all* density matrices of the electron-positron field in the self-consistent quantization.

2. Definition of the Model

The notation and estimates used are mainly those of Barbaroux, Farkas, Helffer, and Siedentop [3]. For the convenience of the reader we give here nevertheless their main definitions and results. The technical tools from [3] are listed in an appendix. For any further details we refer the reader to [3].

The Coulomb-Dirac operator is written as

$$D_g := -\mathrm{i}\boldsymbol{\alpha}\cdot\nabla + \beta - g|\cdot|^{-1}.$$

Physically $g = Z\alpha$ where α is the Sommerfeld fine structure constant and Z is the atomic number of the considered element. The operator is essentially self-adjoint on $\mathcal{S}(\mathbb{R}^3)\otimes\mathbb{C}^4$ if $g\in[0,\sqrt{3}/2)$.

It is convenient to introduce the set $G := \mathbb{R}^3\times\{1,2,3,4\}$ and the measure $dx := d\mathbf{x}\otimes d\mu$, where $d\mathbf{x}$ is the Lebesgue measure on $\mathbb{R}^3$ and $d\mu$ the counting measure of the set $\{1,2,3,4\}$. We denote the Banach space of trace class operators on $\mathfrak{H}$ by $\mathfrak{S}^1(\mathfrak{H})$. Furthermore,

$$F := \{\gamma\in\mathfrak{S}^1(\mathfrak{H}) | \gamma = \gamma^*,\ D_0\gamma\in\mathfrak{S}^1(\mathfrak{H})\}.$$

Note that Barbaroux et al. [3] use a slightly different definition of the space F. Moreover, F is a Banach space when equipped with the norm $\|\gamma\|_F := \|D_0\gamma\|_1 =$

$\||D_0||\gamma|\|_1$. Finally, we note that $\|\gamma\|_{F,g} := \|D_g\gamma\|_1$ is an equivalent norm for $0 \leq g < \sqrt{3}/2$ because of Lemma 12.

We write the integral kernel of any given $\gamma \in F$ using its eigenvalues λ_n and eigenspinors ξ_n as

$$\gamma(x,y) = \sum_{n=1}^{\infty} \lambda_n \xi_n(x)\overline{\xi_n(y)}.$$

The one-particle density associated to γ is

$$\rho_\gamma(\mathbf{x}) := \sum_{s=1}^{4}\sum_{n=1}^{\infty} \lambda_n |\xi_n(x)|^2.$$

Its electric potential operator is $\phi^{(\gamma)} := \rho_\gamma * |\cdot|^{-1}$. The exchange operator $X^{(\gamma)}$ associated to γ is given by its integral kernel

$$X^{(\gamma)}(x,y) := \gamma(x,y)/|\mathbf{x}-\mathbf{y}|.$$

The total interaction operator is defined as

$$W^{(\gamma)} = \phi^{(\gamma)} - X^{(\gamma)}.$$

The Coulomb scalar product is defined as

$$D(\rho,\sigma) := \frac{1}{2}\int_{\mathbb{R}^3} \mathrm{d}\mathbf{x} \int_{\mathbb{R}^3} \mathrm{d}\mathbf{y} \frac{\overline{\rho(\mathbf{x})}\sigma(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}$$

and the exchange scalar product as

$$E(\gamma,\gamma') := \frac{1}{2}\int_G \mathrm{d}x \int_G \mathrm{d}y \frac{\overline{\gamma(x,y)}\gamma'(x,y)}{|\mathbf{x}-\mathbf{y}|}.$$

The total interaction energy is defined as

$$Q(\gamma,\gamma') := D(\rho_\gamma,\rho_{\gamma'}) - E(\gamma,\gamma')$$

For $\alpha \geq 0$ and $\gamma \in F$ the Dirac-Fock operator is defined as

$$D_{g,\alpha}^{(\gamma)} := D_g + \alpha W^{(\gamma)}.$$

Some useful properties of the operators defined above are listed in Appendix B.

For $N \in \mathbb{N}$ and $\delta \in F$ we define

$$\begin{aligned} \widetilde{\mathcal{S}}_{\partial N}^{(\delta)} :=& \{\gamma \in F \,|\, -\Lambda_-^{(\delta)} \leq \gamma \leq \Lambda_+^{(\delta)}, \operatorname{tr}\gamma = N\}, \\ \widetilde{\mathcal{S}}^{(\delta)} :=& \{\gamma \in F \,|\, -\Lambda_-^{(\delta)} \leq \gamma \leq \Lambda_+^{(\delta)}\}, \\ S_N :=& \{\gamma \in F \,|\, 0 \leq \gamma,\ \operatorname{tr}\gamma \leq N\}, \end{aligned}$$

and

$$\mathcal{E}_{g,\alpha}(\gamma) := \operatorname{tr} D_g\gamma + \alpha Q(\gamma,\gamma)$$

where $\Lambda_+^{(\delta)} = \chi_{[0,\infty)}(D_{g,\alpha}^{(\delta)})$ is the projector on the positive spectral subspace of $D_{g,\alpha}^{(\delta)}$ and $\Lambda_-^{(\delta)} = 1 - \Lambda_+^{(\delta)}$ is the projector onto the negative spectral subspace.

Moreover, we will frequently use the abbreviations

$$c_{g,\alpha,N} := (b_g - 4\alpha N)^{-1}, \quad \tilde{c}_{g,\alpha,N} := (\pi/4)\alpha N c_{g,\alpha,N}$$

where $b_g := \sqrt{1-g^2}(\sqrt{4g^2+9} - 4g)/3$ (see also Lemma 12). We denote by ϵ_j^0 and $\epsilon_j^{(\gamma)}$ ($j = 1, \dots$) the eigenvalues of D_g and $D_{g,\alpha}^{(\gamma)}$ respectively (ordered by size and counting multiplicities).

We will be interested in solutions of the Dirac-Fock equations.

Definition 1. *We denote the set of solutions to the Dirac-Fock equations by DF, i.e.,*

$$DF := \{\gamma \in F | \gamma = \gamma^2,\ [D_{g,\alpha}^{(\gamma)}, \gamma] = 0,\ \gamma\Lambda_+^{(\gamma)} = \gamma\}.$$

For fixed g and small α we get: for closed shell atoms there exists a solution $\delta \in DF$ such δ is the projection onto the first N positive eigenvalue of $D_{g,\alpha}^{(\delta)}$ (Theorem 1). We will prove this result using the Banach fixed point theorem yielding even uniqueness of the solution. We also show that the fixed point (Corollary 3) and the energy functional $\mathcal{E}_{g,\alpha}$ (Theorem 2) are spherically symmetric in a certain sense, and that the fixed point minimizes $\mathcal{E}_{g,\alpha}$ on DF (Corollary 2). To this end the uniqueness of the fixed point is crucial.

Moreover, we show (Theorem 3) that this solution minimizes $\mathcal{E}_{g,\alpha}$ even on the set $\widetilde{\mathcal{S}}_{\partial q}^{(\delta)}$ We emphasize that we do not need to require $\Lambda_+^{(\delta)}\gamma\Lambda_-^{(\delta)} = 0$, a fact that had to be left open in the context of the no-pair Hartree-Fock theory discussed in [3].

Note, that the notion of closed shells – as used in this article – refers to the Coulomb-Dirac operator, i.e., for $N \in \mathbb{N}$ we are in the closed shell case, if $\epsilon_{N+1}^0 > \epsilon_N^0$. It does not matter, if the gap is the gap between shells with different principal quantum numbers. This means that $N = 2, 8, 10, ...$ For brevity, we denote the set of all such N by CS.

3. Controlling the Spectrum of Dirac-Fock Operators

The aim of this section is to derive some estimates which control the eigenvalues of Dirac-Fock operators by the corresponding eigenvalues of Coulomb-Dirac operators. The main tool of this section is the minimax principle of Griesemer and Siedentop [8], which is formulated in Appendix A (Theorem 4). We are going to use the Coulomb-Dirac operator as unperturbed operator and the Dirac-Fock operator as perturbed operator. First, we check the hypotheses of the minimax theorem (Theorem 4).

Lemma 1. *Let $A = D_{g,\alpha}^{(\gamma)}$ with $0 \leq \gamma \in F$, $\mathfrak{h} = L^2(\mathbb{R}^3)^4$, $\mathfrak{Q} = \mathcal{D}(A)$. Let $\Lambda_+ := \chi_{(0,\infty)}(D_g)$, $\Lambda_- := \chi_{(-\infty,0)}(D_g)$, and $\mathfrak{h}_\pm := \Lambda_\pm\mathfrak{h}$ and assume $0 \notin \sigma(D_{g,\alpha}^{(\gamma)})$. Then the hypotheses of Theorem 4 are fulfilled, if $(\pi/2)\alpha\|\gamma\|_1 \leq b_g$.*

Proof. Let $f \in \mathfrak{Q}_-$. Then

$$\begin{aligned}(f, D_{g,\alpha}^{(\gamma)}f) &= (f, D_g f) + \alpha(f, W^{(\gamma)}f) \leq (f, D_g f) + \alpha(f, \phi^{(\gamma)}f)\\ &\leq (f, D_g f) + \frac{\pi}{2}\alpha\|\gamma\|_1(f, |\nabla| f) \leq (f, D_g f) + \frac{\pi}{2}\alpha\|\gamma\|_1\frac{1}{b_g}(f, |D_g| f) \leq 0\end{aligned}$$

where we used Lemmata 8 and 12, and (17),. The condition

$$(f, D_{g,\alpha}^{(\gamma)}f) > 0$$

for all $f \in \mathcal{Q}(A) \cap \mathfrak{H}_+$ is trivially fulfilled since $W^{(\gamma)} \geq 0$ (Lemma 8). It remains to check the boundedness of $(|D_{g,\alpha}^{(\gamma)}| + 1)^{\frac{1}{2}} P_- \Lambda_+$. To this end we proceed as follows: As in [7, Lemma 1],

$$P_-\Lambda_+ = -\frac{\alpha}{2\pi}\int_{-\infty}^{\infty}(D_{g,\alpha}^{(\gamma)} - \mathrm{i}\eta)^{-1}W^{(\gamma)}(D_g - \mathrm{i}\eta)^{-1}\mathrm{d}\eta\Lambda_+,$$

i.e., we have to estimate the expression

$$\int_{-\infty}^{\infty}(|D_{g,\alpha}^{(\gamma)}| + 1)^{\frac{1}{2}}(D_{g,\alpha}^{(\gamma)} - \mathrm{i}\eta)^{-1}W^{(\gamma)}(D_g - \mathrm{i}\eta)^{-1}\mathrm{d}\eta.$$

Now, $\|(D_g - \mathrm{i}\eta)^{-1}\| \leq [(\epsilon_1^0)^2 + \eta^2]^{-1/2}$. Moreover, we look at the function

$$[\lambda_0, \infty) \to \mathbb{R}, f_\eta(\lambda) := \sqrt{(\lambda + 1)/(\lambda^2 + \eta^2)}$$

where $\lambda_0 := \inf \sigma(|D_{g,\alpha}^{(\gamma)}|) > 0$ by assumption. This function has its maximum at the point $\max\{\lambda_0, -1+\sqrt{1+\eta^2}\}$, i.e.,

$$\sup_\lambda f_\eta(\lambda) = \begin{cases} \sqrt{(\lambda_0+1)/(\lambda_0^2+\eta^2)} & |\eta| \leq \sqrt{(\lambda_0+1)^2-1} \\ \sqrt{\frac{(-1+\sqrt{1+\eta^2})+1}{(-1+\sqrt{1+\eta^2})^2+\eta^2}} & |\eta| > \sqrt{(\lambda_0+1)^2-1}. \end{cases}$$

We conclude that

$$\int_{-\infty}^{\infty} \|(|D_{g,\alpha}^{(\gamma)}|+1)^{1/2}(D_{g,\alpha}^{(\gamma)} - \mathrm{i}\eta)^{-1}\| \|W^{(\gamma)}\| \|(D_g - \mathrm{i}\eta)^{-1}\| \mathrm{d}\eta$$

is finite, which implies the boundedness of $(|D_{g,\alpha}^{(\gamma)}|+1)^{\frac{1}{2}} P_- \Lambda_+$. □ □

Lemma 12 shows that the condition $0 \in \rho(D_{g,\alpha}^{(\gamma)})$ in Lemma 1 is fulfilled, if $b_g > 4\alpha\|\gamma\|_1$. One can relax this condition adapting an argument of Barbaroux et al. ([4]); but since it is not the most restrictive condition, we refrain from doing so.

Lemma 1 enables us to control the eigenvalues of the Dirac-Fock operator by the eigenvalues of the Coulomb-Dirac operator. Since the minimax principle yields the eigenvalues ordered by size and counting multiplicities, we do not only get some information on the localization of the eigenvalues but also on the dimension of the projector onto a given part of the discrete spectrum. Note that the estimate depends only on $\|\gamma\|_1$ but not on γ itself.

Lemma 2. *Let $0 \leq \gamma \in F$ and let the hypotheses of Lemma 1 be fulfilled. Then, for all $n \in \mathbb{N}$*

$$\epsilon_n^0 \leq \epsilon_n^{(\gamma)} \leq (1 + (\pi/2)\alpha\|\gamma\|_1 b_g^{-1})\epsilon_n^0.$$

Proof. Since $0 \leq X^{(\gamma)}$, $0 \leq \phi^{(\gamma)}$ and $0 \leq W^{(\gamma)}$ (Lemma 8), we have using (17) and Lemma 12

$$\begin{aligned} D_g &\leq D_g + \alpha W^{(\gamma)} \leq D_g + \alpha\phi^{(\gamma)} \leq D_g + \tfrac{\pi}{2}\alpha\|\gamma\|_1|\nabla| \\ &\leq D_g + \tfrac{\pi}{2}\alpha\|\gamma\|_1 b_g^{-1}|D_g| \leq (1+\tfrac{\pi}{2}\alpha\|\gamma\|_1 b_g^{-1})(D_g)_+ + (1-\tfrac{\pi}{2}\alpha\|\gamma\|_1 b_g^{-1})(D_g)_- \end{aligned}$$

where $(D_g)_+$ and $(D_g)_-$ denote the positive and negative part of the Coulomb-Dirac operator respectively. We choose now $\mathfrak{h}_\pm := \Lambda_\pm\mathfrak{h}$. Then the above operator inequality yields immediately for all $n \in \mathbb{N}$ the inequality $\lambda_n(D_g) \leq \lambda_n(D_{g,\alpha}^{(\gamma)}) \leq (1+(\pi/2)\alpha\|\gamma\|_1 b_g^{-1})\lambda_n(D_g)$, where the λ_n are the minimax values defined in Theorem 4. Now, by Lemma 1 the hypotheses of Theorem 4 are fulfilled for $D_{g,\alpha}^{(\gamma)}$. For D_g the hypotheses are trivially fulfilled by the choice of $\mathfrak{h}_\pm := \Lambda_\pm\mathfrak{h}$. For the operator $(1+(\pi/2)\alpha\|\gamma\|_1/d_g)(D_g)_+ + (1-(\pi/2)\alpha\|\gamma\|_1/d_g)(D_g)_-$ the hypotheses are also fulfilled, since it has got the same positive and negative spectral subspaces as the operator D_g. Thus Theorem 4 immediately yields the claimed inequality. □ □

Lemma 3. *Let $0 \leq \gamma \in F$ with ρ_γ spherically symmetric and let the hypotheses of Lemma 1 be fulfilled. Then, for all $n \in \mathbb{N}$*

$$\epsilon_n^0 \leq \epsilon_n^{(\gamma)} \leq \epsilon(g - \alpha\|\gamma\|_1)_n^0,$$

where $\epsilon(g-\alpha\|\gamma\|_1)_n^0$ denote the eigenvalues of the Coulomb-Dirac operator with g replaced by $g - \alpha\|\gamma\|_1$.

Proof. The first inequality is the same as in Lemma 2. For the second inequality note that $\phi^{(\gamma)} \leq \|\gamma\|_1|\cdot|^{-1}$ by Newton's inequality. Thus, by Lemma 8

$$D_{g,\alpha}^{(\gamma)} = D_g + \alpha\phi^{(\gamma)} - \alpha X^{(\gamma)} \leq D_g + \alpha\|\gamma\|_1|\cdot|^{-1}.$$

Since

$$(f, (D_0 - g|\cdot|^{-1} + \alpha\|\gamma\|_1|\cdot|^{-1})f) = (f, D_{g-\alpha\|\gamma\|_1} f) \leq 0$$

by Kato's inequality and Lemma 12 for all $f \in \mathfrak{Q}_-$, we get by the Minimax Theorem 4

$$\lambda_n(D_{g-\alpha\|\gamma\|_1}) \leq \epsilon(g-\alpha\|\gamma\|_1)^0_n.$$

Using Lemma 1, this implies the claim. □ □

We define now $c := (1+(\pi/2)\alpha N/b_g)\epsilon^0_N$ and $\eta := \epsilon^0_{N+1} - c = \epsilon^0_{N+1} - (1 + (\pi/2)\alpha N/b_g)\epsilon^0_N$. Let

$$\alpha_0 := \sup\{\alpha \in \mathbb{R} | \epsilon^0_{N+1} - (1+\tfrac{\pi}{2}\alpha N/b_g)\epsilon^0_N > 0\} = 2(\epsilon^0_{N+1} - \epsilon^0_N)b_g/(\pi N \epsilon^0_N).$$

To simplify the notation, the dependence of these quantities on g and α is suppressed. Eventually, we set

$$\begin{aligned} g_{g,N}(\alpha) := {} & (\epsilon^0_N)^2\pi^2N^3\alpha^3 + [-6\pi N^2\epsilon^0_N\epsilon^0_{N+1} + \left(4\pi - 1/4\pi^2\right)N^2(\epsilon^0_N)^2]b_g\alpha^2 \\ & + [(\pi-12)N\epsilon^0_N\epsilon^0_{N+1} - 4N\epsilon^0_1\epsilon^0_N + 12n(\epsilon^0_{N+1})^2 + (4-\pi)N(\epsilon^0_N)^2]{b_g}^2\alpha \\ & - {b_g}^3(\epsilon^0_N + \epsilon^0_{N+1})^2 \end{aligned}$$

and define α_0' be the smallest root of the cubic equation $g_{g,N}(\alpha) = 0$. Furthermore, $Z \leq \alpha^{-1}_{\mathrm{phys}}\sqrt{1-(1+\sqrt{33})/16)^2} \approx 124.23$ implies $\epsilon^0_1 \geq \epsilon^0_3 - \epsilon^0_1$ holds, so that $\epsilon^0_1 \geq \eta$ is fulfilled for these values of Z.

Theorem 1. *Assume $N \in CS$ and $\alpha < \min\{\alpha_0, \alpha_0', b_g/(4N)\}$. We pick a path C as*

$$C(t) := \begin{cases} \epsilon^0_1 - \frac{\eta}{2} + t(c + \frac{\eta}{2} - (\epsilon^0_1 - \frac{\eta}{2})) - \mathrm{i}\frac{\eta}{2} & 0 \leq t \leq 1 \\ c + \frac{\eta}{2} - \mathrm{i}\frac{\eta}{2} + (t-1)\eta & 1 \leq t \leq 2 \\ c + \frac{\eta}{2} + (t-2)(\epsilon^0_1 - \frac{\eta}{2} - (c+\frac{\eta}{2})) + \mathrm{i}\frac{\eta}{2} & 2 \leq t \leq 3 \\ \epsilon^0_1 - \frac{\eta}{2} + \mathrm{i}\frac{\eta}{2} - \mathrm{i}(t-3)\eta & 3 \leq t \leq 4. \end{cases}$$

Then the mapping

$$T : S_N \to S_N,\ \gamma \mapsto -(2\pi\mathrm{i})^{-1}\int_C (D^{(\gamma)}_{g,\alpha} - z)^{-1}\mathrm{d}z$$

has a unique fixed point.

We remark that our bound on the range of allowed fine structure constants α in the hypothesis tends to zero as $1/N$. This has one main technical reason: the control on eigenvalues of the Dirac-Fock operator in terms of the Coulomb-Dirac operator becomes worse as the particle number grows, since the gap between the eigenvalues becomes smaller for larger eigenvalues (see Lemma 2). This is also the reason why our estimates on the contraction properties of the map T becomes worse as N growths.

Proof. Step 1: Note that S_N is a closed subset of F. Pick $\gamma \in S_N$. Because of the inequalities (Lemma 2)

$$\epsilon^0_1 \leq \epsilon^0_k \leq \epsilon^{(\gamma)}_k \leq (1+\tfrac{\pi}{2}\alpha N b_g^{-1})\epsilon^0_k \leq (1+\tfrac{\pi}{2}\alpha N b_g^{-1})\epsilon^0_N < \epsilon^0_{N+1}$$

for $k = 1, \ldots, N$ and because $T(\gamma)$ is the projector onto the spectral subspace of $D^{(\gamma)}_{g,\alpha}$ corresponding to the N lowest eigenvalues of $D^{(\gamma)}_{g,\alpha}$ (Reed and Simon [12, Theorem XII.6]) we have $\gamma \in F$, $\mathrm{tr}\, T(\gamma) = N$ and $\gamma \geq 0$. Thus, T is well defined.

Step 2: We show that the mapping T is a contraction: pick $\gamma, \gamma' \in S_N$. Let P be the projector on range$(|D_g|(T(\gamma) - T(\gamma'))$. Since dim range$((T(\gamma) - T(\gamma')) \leq 2N$, we have $\dim\operatorname{range}(|D_g|(T(\gamma)-T(\gamma'))\leq 2N$, implying $\|P\|_1\leq 2N$. Thus,

$$\begin{aligned}\|T(\gamma)-T(\gamma')\|_{F,g} &= \||D_g|(T(\gamma)-T(\gamma'))\|_1 = \|P|D_g|(T(\gamma)-T(\gamma'))\|_1\\ &\leq \|P\|_1\||D_g|(T(\gamma)-T(\gamma'))\| \leq \frac{2N}{1-4\alpha N/b_g}\||D_{g,\alpha}^{(\gamma)}|(T(\gamma)-T(\gamma'))\|\\ &\leq 2Nc_{g,\alpha,N}b_g\||D_{g,\alpha}^{(\gamma)}|(T(\gamma)-T(\gamma'))\|\\ &\leq \pi^{-1}c_{g,\alpha,N}b_gN\||D_{g,\alpha}^{(\gamma)}|\int_C(D_{g,\alpha}^{(\gamma)}-z)^{-1}-(D_{g,\alpha}^{(\gamma')}-z)^{-1}\mathrm{d}z\|\\ &\leq \frac{\alpha c_{g,\alpha,N}Nb_g}{\pi}\|\int_C|D_{g,\alpha}^{(\gamma)}|(D_{g,\alpha}^{(\gamma)}-z)^{-1}W^{(\gamma-\gamma')}(D_{g,\alpha}^{(\gamma')}-z)^{-1}\mathrm{d}z\|\\ &\leq \alpha c_{g,\alpha,N}N(2\eta+(c-\epsilon_1^0))\times\\ &\max_{z\in C([0,4])}(\||D_{g,\alpha}^{(\gamma)}|(D_{g,\alpha}^{(\gamma)}-z)^{-1}\|)\max_{z\in C([0,4])}\|(D_{g,\alpha}^{(\gamma')}-z)^{-1}\|\|\gamma-\gamma'\|_{F,g}\end{aligned}$$

where we used Lemma 12, the resolvent identity, Lemma 7 and (16).

Pick an arbitrary $z=x+iy\in\mathbb{C}$ $(x,y\in\mathbb{R})$. We derive estimates for $\||D_{g,\alpha}^{(\gamma)}|(D_{g,\alpha}^{(\gamma)}-z)^{-1}\|$. Let $A:=\mathbb{R}\setminus[(0,\epsilon_1^0)\cup(c,\epsilon_{N+1}^0)]$ and E the spectral resolution of $D_{g,\alpha}^{(\gamma)}$. Because $E[(0,\epsilon_1^0)\cup(c,\epsilon_{N+1}^0)]=0$, it follows that

$$\||D_{g,\alpha}^{(\gamma)}|(D_{g,\alpha}^{(\gamma)}-z)^{-1}\|\leq\sup_{\lambda\in A}|\lambda|/|\lambda-z|=\sup_{\lambda\in A}f_{x,y}(\lambda)$$

where

$$f_{x,y}(\lambda):=|\lambda|/|\lambda-z|=|\lambda|((\lambda-x)^2+y^2)^{-1/2}.$$

First assume $x=c+\eta/2$ and y arbitrary. Since $f_{x,y}(\lambda)\leq|\lambda|/|\lambda-x|$, we get

$$\sup_{\lambda\in A}f_{x,y}(\lambda)\leq|\epsilon_{N+1}^0|/|\epsilon_{N+1}^0-x|=2\epsilon_{N+1}^0/\eta.$$

Similarly for $x=\epsilon_1^0-\eta/2$ and arbitrary y, we get

$$\||D_{g,\alpha}^{(\gamma)}|(D_{g,\alpha}^{(\gamma)}-z)^{-1}\|\leq 2\epsilon_1^0/\eta.$$

Now let $y=\pm\eta/2$ and $x\in[\epsilon_1^0-\eta/2,c+\eta/2]$. Obviously with $B:=[\epsilon_1^0,c]\cup[\epsilon_{n+1}^0,\infty)$,

$$\sup_{\lambda\in A}f_{x,y}(\lambda)=\sup_{\lambda\in B}f_{x,y}(\lambda).$$

A little calculation shows that $f_{x,y}$ attains its maximum on $[0,\infty)$ at $\lambda_0=(x^2+y^2)/x$. Moreover, $f_{x,y}(\lambda)\leq|\lambda|/|y|$ for all $\lambda\in\mathbb{R}$, implying

$$\||D_{g,\alpha}^{(\gamma)}|(D_{g,\alpha}^{(\gamma)}-z)^{-1}\|\leq f_{x,y}(\lambda_0)\leq(x^2+y^2)/(x|y|).$$

Since the function $h_y(b):=(b^2+y^2)/(b|y|)$ attains its minimum on $(0,\infty)$ at $b=|y|$ and is monotonously increasing for $b>|y|$, we get

$$\||D_{g,\alpha}^{(\gamma)}|(D_{g,\alpha}^{(\gamma)}-z)^{-1}\|\leq[(c+\eta/2)^2+\eta^2/4]/[(c+\eta/2)\eta/2],$$

because $x>y$ by the remark before the theorem. Now a little calculation shows that

$$\frac{(c+\eta/2)^2+(\eta/2)^2}{(c+\eta/2)\eta/2}\leq\frac{2\epsilon_{N+1}^0}{\eta}$$

implying $\||D_{g,\alpha}^{(\gamma)}|(D_{g,\alpha}^{(\gamma)}-z)^{-1}\|\leq 2\epsilon_{N+1}^0/\eta$ for all $z\in C([0,4])$. We also use

$$\|(D_{g,\alpha}^{(\gamma')}-z)^{-1}\|\leq 1/\operatorname{dist}(z,\sigma(D_{g,\alpha}^{(\gamma')}))=2/\eta$$

for $z\in\rho(D_{g,\alpha}^{(\gamma')})$ yielding altogether

$$\begin{aligned}\|T(\gamma)-T(\gamma')\|_{F,g}\leq&\alpha c_{g,\alpha,N}N\cdot(2\eta+(c-\epsilon_1^0))2\epsilon_{N+1}^0\eta^{-1}2\eta^{-1}\|\gamma-\gamma'\|_{F,g}\\ =&\alpha[4Nc_{g,\alpha,N}\epsilon_{n+1}^0(2\eta+(c-\epsilon_1^0))]\eta^{-2}\|\gamma-\gamma'\|_{F,g}.\end{aligned}$$

Now the condition $4\alpha N c_{g,\alpha,N}\epsilon^0_{N+1}(2\eta + (c-\epsilon^0_1))\eta^{-2} < 1$ leads to the inequality $g_{g,N}(\alpha) < 0$ which proves the claim. □ □

Note that the set of density matrices $\gamma \in F$ with spherical density ρ_γ is closed in the F-norm: taking a F-convergent sequence γ_n of such density matrices we merely have to show that the limiting density matrix has spherical density, too. However, convergence in F implies convergence of the corresponding densities ρ_n in L^1. Suppose that R is a rotation, then $\rho_{n,R}(x) := \rho_n(Rx) \stackrel{a.e.}{=} \rho_n(x)$. Thus, also $L^1\text{–}\lim_{n\to\infty}\rho_n = L^1\text{–}\lim_{n\to\infty}\rho_{n,R}$. Thus we may apply the fixed point theorem to this smaller set. This improves the estimates in the proof Theorem 1 slightly using Lemma 3. We display the result of a numerical evaluation of the corresponding – more complicated condition – in Figure 1.

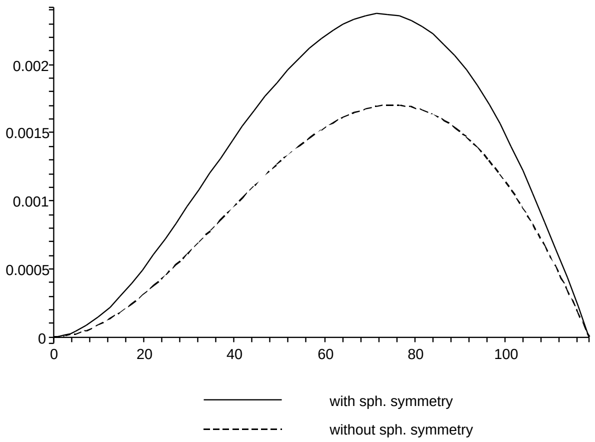

FIGURE 1. The maximal value of α, for which the contraction property of T can be guaranteed, in dependence on the nuclear charge $Z = 137g$ for $N = 2$ with and without assuming spherical symmetry. (Note: in our proves we use – because of theoretical reasons – two independent parameters, namely g and α. Physically, one would choose: (i) $g = \alpha_{\text{phys}} Z$ where Z is the atomic number of the considered element. (ii) $\alpha = \alpha_{\text{phys}}$ where $\alpha_{\text{phys}} \approx 1/137$. To make contact with the physics, we make this first choice and plot the maximal value of α fulfilling our hypotheses. The plot shows that we do not reach α_{phys}; however, our result is on the right order of magnitude for highly ionized medium sized atoms.)

Corollary 1. *If $N \in CS$ and α fulfills the hypotheses of Theorem 1, then there exists a unique $\delta \in F$ which is the projector onto the eigenspace of the N lowest eigenvalues of $D^{(\delta)}_{g,\alpha}$.*

Proof. Theorem 1 ensures the existence of such a δ. On the other hand, any projector γ onto the N lowest positive eigenvalues of $D^{(\gamma)}_{g,\alpha}$, fulfills the equation $T(\gamma) = \gamma$ which has the unique solution δ. □ □

We set

$$E_N := \epsilon^0_1 + \ldots + \epsilon^0_{N-1} \qquad a := 2\pi N^2(E_N + \epsilon^0_N)$$
$$b := [-\tfrac{3}{4}\pi E_N - (4+\tfrac{\pi}{4})\epsilon^0_{N+1} + (4-\tfrac{\pi}{2})\,\epsilon^0_N]b_g N \qquad c := (-\epsilon^0_N + \epsilon^0_{N+1})b_g^2$$
$$a_{g,N} := (-b - \sqrt{b^2 - 4ac})/(2a).$$

Corollary 2. *If $N \in CS$ and there is a unique solution δ of the equation $T(\gamma) = \gamma$, then it minimizes the energy among all Dirac-Fock solutions, i.e., this solution fulfills*

$$\mathcal{E}_{g,\alpha}(\delta) = \min\{\mathcal{E}_{g,\alpha}(\gamma) | \gamma \in DF,\ \operatorname{tr}\gamma = N\},$$

if $\alpha \le \min\{a_{g,N}, b_g/(4N), \alpha_0\}$.

Proof. Because of Lemma 9 we have for all $\gamma \ge 0$

$$\mathcal{E}_{g,\alpha}(\gamma) = \operatorname{tr} D_{g,\alpha}^{(\gamma)}\gamma - \alpha Q(\gamma,\gamma) \le \operatorname{tr} D_{g,\alpha}^{(\gamma)}\gamma. \tag{1}$$

We pick an arbitrary solution γ of (DF) with $\operatorname{tr}\gamma = N$. With Lemma 9 and 12 we get

$$\begin{aligned}
\mathcal{E}_{g,\alpha}(\gamma) &= \operatorname{tr} D_{g,\alpha}^{(\gamma)}\gamma - \alpha Q(\gamma,\gamma) \ge \operatorname{tr} D_{g,\alpha}^{(\gamma)}\gamma - \alpha D(\rho_\gamma,\rho_\gamma)\\
&\ge \operatorname{tr} D_{g,\alpha}^{(\gamma)}\gamma - \tfrac{\pi}{4}\alpha N \operatorname{tr}|\nabla||\gamma| \ge \operatorname{tr} D_{g,\alpha}^{(\gamma)}\gamma - \tfrac{\pi}{4}\alpha N c_{g,\alpha,N} \operatorname{tr}|D_{g,\alpha}^{(\gamma)}||\gamma|\\
&= (1-\tilde{c}_{g,\alpha,N}) \operatorname{tr} D_{g,\alpha}^{(\gamma)}\gamma.
\end{aligned} \tag{2}$$

We denote by ϵ_k, $k = 1,\dots,N$, the eigenvalues (ordered by size and counting multiplicities) of $D_{g,\alpha}^{(\gamma)}$ whose eigenvectors are in the range of γ. If the ϵ_k, $k = 1,\dots,N$, fulfill the inequality

$$\epsilon_1^0 \le \epsilon_k \le \left(1 + \tfrac{\pi}{2}\alpha N b_g^{-1}\right)\epsilon_N^0$$

for $k = 1,\dots,N$, the γ is a projector onto the eigenspace of the N lowest eigenvalues of $D_{g,\alpha}^{(\gamma)}$ and hence equal to the unique fixed point δ of T. By equation (1) and Lemma 2, we get for the energy of the fixed point

$$\mathcal{E}_{g,\alpha}(\delta) \le \sum_{m=1}^{N} \epsilon_m^{(\delta)} \le (1 + \tfrac{\pi}{2}\alpha N b_g^{-1}) \sum_{m=1}^{N} \epsilon_m^0.$$

If, on the other hand, there is a $l \in \{1,\dots,N\}$ such that $\epsilon_j \ge \epsilon_{N+1}^{(0)}$ for all $j \ge l$ and $\epsilon_j \le (1 + \frac{\pi}{2}\alpha N b_g^{-1})\epsilon_n^{(0)}$ for all $j \le l-1$, then, by (2), we get

$$\begin{aligned}
\mathcal{E}_{g,\alpha}(\gamma) &\ge (1-\tilde{c}_{g,\alpha,N}) \operatorname{tr} D_{g,\alpha}^{(\gamma)}\gamma = (1-\tilde{c}_{g,\alpha,N}) \sum_{m=1}^{N} \epsilon_m\\
&\ge (1-\tilde{c}_{g,\alpha,N})\Big(\sum_{m=1}^{l-1}\epsilon_m^0 + \sum_{m=l}^{N}\epsilon_m\Big) \ge (1-\tilde{c}_{g,\alpha,N})\Big(\sum_{m=1}^{N-1}\epsilon_m^0 + \epsilon_{N+1}^0\Big).
\end{aligned}$$

Now, because $\epsilon_m \ge \epsilon_{N+1}^{(0)} > \epsilon_N^{(0)}$ for $m \ge l$, it follows that

$$\begin{aligned}
&\mathcal{E}_{g,\alpha}(\gamma) - \mathcal{E}_{g,\alpha}(\delta)\\
&\quad = (1-\tilde{c}_{g,\alpha,N}) \sum_{m=1}^{N-1}\epsilon_m^0 + (1-\tilde{c}_{g,\alpha,N})\epsilon_{N+1}^0 - (1 + \tfrac{\pi}{2}\alpha\tfrac{N}{b_g}) \sum_{m=1}^{N}\epsilon_m^0\\
&\quad = -\alpha(\tfrac{\pi}{4}N c_{g,\alpha,N} + \tfrac{\pi N}{2b_g}) \sum_{m=1}^{N-1}\epsilon_m^0 + (1 - \tfrac{\pi}{4}\alpha N c_{g,\alpha,N})\epsilon_{N+1}^0 - (1 + \tfrac{\pi}{2}\alpha\tfrac{N}{b_g})\epsilon_N^0.
\end{aligned}$$

The condition $\mathcal{E}_{g,\alpha}(\gamma) - \mathcal{E}_{g,\alpha}(\delta) \ge 0$ yields the quadratic equation in α

$$\begin{aligned}
2\pi N^2(E_N + \epsilon_N^0)\alpha^2 + \left[-\tfrac{3\pi}{4}E_N - \left(4 + \tfrac{\pi}{4}\right)\epsilon_{n+1}^0 + (4 - \tfrac{\pi}{2})\epsilon_N^0\right] b_g N\alpha&\\
+ \left(-\epsilon_N^0 + \epsilon_{N+1}^0\right) b_g^2 = 0,&
\end{aligned}$$

whose smallest root $a_{g,N}$ is relevant. □ □

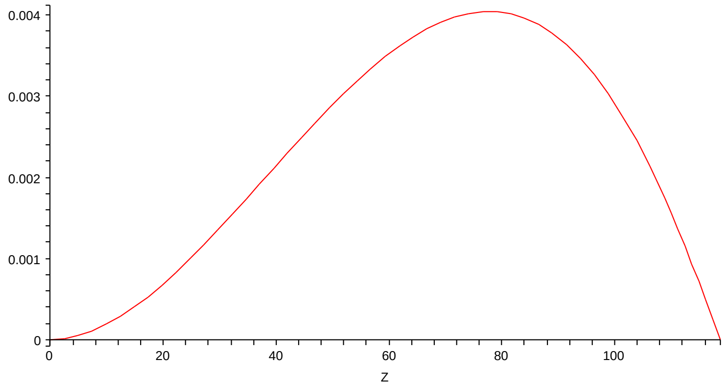

FIGURE 2. The constant $\min\{a_{g,n}, b_g/(4N), \alpha_0\}$ in dependence on the nuclear charge $Z = 137g$ for $N = 2$.

4. SPHERICAL SYMMETRY

As a next step – following [2] – we show that the fixed point of T is spherically symmetric in a certain sense: For any $R \in SO(3)$ there is a $U_R \in SU(2)$ such that $(R\mathbf{x})\cdot\vec{\sigma} = U_R(\mathbf{x}\cdot\vec{\sigma})U_R^{-1}$ for all $\mathbf{x} \in \mathbb{R}^3$. Note that U_R is not unique; the two possible choices differ only by -1. Since we are only interested in eigenvectors, we do not care about this ambiguity. Pick

$$f = \begin{pmatrix} f^{(u)} \\ f^{(l)} \end{pmatrix} \in L^2(\mathbb{R}^3; \mathbb{C}^4).$$

We define

$$f_R(\mathbf{x}) = \begin{pmatrix} U_R f^{(u)}(R^{-1}\mathbf{x}) \\ U_R f^{(l)}(R^{-1}\mathbf{x}) \end{pmatrix}.$$

Obviously, $f_R \in L^2(\mathbb{R}^3; \mathbb{C}^4)$. For $\gamma = \sum_{n=1}^\infty \lambda_n |\xi_n\rangle\langle\xi_n| \in F$ we define

$$\gamma_R := \sum_{n=1}^\infty \lambda_n |(\xi_n)_R\rangle\langle(\xi_n)_R|.$$

We first show the following

Lemma 4. *If $f \in L^2(\mathbb{R}^3; \mathbb{C}^4)$ is an eigenfunction of $D_{g,\alpha}^{(\gamma)}$ with eigenvalue ϵ, then $f_R \in L^2(\mathbb{R}^3; \mathbb{C}^4)$ is eigenfunction of $D_{g,\alpha}^{(\gamma_R)}$ with eigenvalue ϵ.*

Proof. We treat the Dirac-Fock operator term by term.

Step 1: Let $Q = R^{-1}$. We have

$$(-i\boldsymbol{\alpha}\cdot\nabla f_R)(x) = V_R(-i\boldsymbol{\alpha}\cdot\nabla f)(Qx) \tag{3}$$

where

$$V_R = \begin{pmatrix} U_R & 0 \\ 0 & U_R \end{pmatrix}.$$

Proof of Step 1: We denote by ∂ the total derivative and by ∂_j the respective partial derivatives.

$$\partial_j f_R = \begin{pmatrix} U_R \partial_j f_R^{(u)} \\ U_R \partial_j f_R^{(d)} \end{pmatrix} = \begin{pmatrix} U_R[(\partial f^{(u)})\circ Q]Qe_j \\ U_R[(\partial f^{(l)})\circ Q]Qe_j \end{pmatrix} = \begin{pmatrix} U_R \sum_{k=1}^3 [(\partial_k f^{(u)})\circ Q]Q_{kj} \\ U_R \sum_{k=1}^3 [(\partial_k f^{(l)})\circ Q]Q_{kj} \end{pmatrix}$$

It follows that

$$\boldsymbol{\alpha}\cdot\nabla f_R = \sum_{j=1}^{3}\sum_{k=1}^{3}\begin{pmatrix}\sigma_j U_R[(\partial_k f^{(l)})\circ Q]Q_{kj}\\ \sigma_j U_R[(\partial_k f^{(u)})\circ Q]Q_{kj}\end{pmatrix}$$

$$= \sum_{k=1}^{3}\begin{pmatrix}U_R U_R^{-1}(\vec\sigma\cdot Re_k)U_R(\partial_k f^{(l)})\circ Q\\ U_R U_R^{-1}(\vec\sigma\cdot Re_k)U_R(\partial_k f^{(u)})\circ Q\end{pmatrix} = \sum_{k=1}^{3}\begin{pmatrix}U_R\sigma_k(\partial_k f^{(l)})\circ Q\\ U_R\sigma_k(\partial_k f^{(u)})\circ Q\end{pmatrix}$$

$$= V_R(\boldsymbol{\alpha}\cdot\nabla f)\circ Q$$

Second term: We have

$$\beta f_R = \beta\begin{pmatrix}U_R & 0\\ 0 & U_R\end{pmatrix}\begin{pmatrix}f^{(u)}\circ Q\\ f^{(l)}\circ Q\end{pmatrix} = V_R(\beta f)\circ Q \tag{4}$$

Third term:

$$|\cdot|^{-1}f_R = V_R|Q\cdot|^{-1}f\circ Q = V_R|\cdot|^{-1}f\circ Q \tag{5}$$

Fourth term:

$$\phi^{(\gamma_R)}f_R = V_R\Big[\sum_n \lambda_n\Big\langle\begin{pmatrix}U_R[\xi_n^{(u)}\circ Q]\\ U_R[\xi_n^{(l)}\circ Q]\end{pmatrix},\begin{pmatrix}U_R[\xi_n^{(u)}\circ Q]\\ U_R[\xi_n^{(l)}\circ Q]\end{pmatrix}\Big\rangle_{\mathbb{C}^4} * \frac{1}{|\cdot|}\Big](f\circ Q) \tag{6}$$

$$= V_R\int\sum_n \lambda_n\Big\langle\begin{pmatrix}\xi_n^{(u)}(\mathbf{y})\\ \xi_n^{(l)}(\mathbf{y})\end{pmatrix},\begin{pmatrix}\xi_n^{(u)}(\mathbf{y})\\ \xi_n^{(l)}(\mathbf{y})\end{pmatrix}\Big\rangle_{\mathbb{C}^4}\frac{\mathrm{d}\mathbf{y}}{|\cdot - R\mathbf{y}|}f\circ Q$$

$$= V_R[(\phi^{(\gamma)}\circ Q)(f\circ Q)] = V_R[(\phi^{(\gamma)}f)\circ Q]$$

Fifth term:

(7) $(X^{(\gamma_R)}f_R)(\mathbf{x})$

$$= \int\sum_n \lambda_n\begin{pmatrix}U_R\xi_n^{(u)}(Q\mathbf{x})\\ U_R\xi_n^{(l)}(Q\mathbf{x})\end{pmatrix}\Big\langle\begin{pmatrix}U_R\xi_n^{(u)}(Q\mathbf{y})\\ U_R\xi_n^{(l)}(Q\mathbf{y})\end{pmatrix},\begin{pmatrix}U_R f^{(u)}(Q\mathbf{y})\\ U_R f^{(l)}(Q\mathbf{y})\end{pmatrix}\Big\rangle_{\mathbb{C}^4}\frac{\mathrm{d}\mathbf{y}}{|\mathbf{x}-\mathbf{y}|}$$

$$= V_R\int\mathrm{d}\mathbf{y}\sum_n\lambda_n\frac{\begin{pmatrix}\xi_n^{(u)}(Q\mathbf{x})\\ \xi_n^{(l)}(Q\mathbf{x})\end{pmatrix}\Big\langle\begin{pmatrix}\xi_n^{(u)}(\mathbf{y})\\ \xi_n^{(l)}(\mathbf{y})\end{pmatrix},\begin{pmatrix}f^{(u)}(\mathbf{y})\\ f^{(l)}(\mathbf{y})\end{pmatrix}\Big\rangle_{\mathbb{C}^4}}{|\mathbf{x}-R\mathbf{y}|}$$

$$= V_R(X^{(\gamma)}f)(Q\mathbf{x})$$

Thus,

$$(D^{(\gamma_R)}f_R)(\mathbf{x}) = V_R(D_{g,\alpha}^{(\gamma)}f)(Q\mathbf{x}) = \epsilon V_R f(Q\mathbf{x}) = \epsilon f_R(\mathbf{x})$$

which proves the claim. □ □

Corollary 3. *If $\alpha < \alpha_0$ and if T has a unique fixed point δ, then*

$$\delta_R = \delta$$

for all $R\in SO(3)$ i.e., δ is spherically symmetric.

Proof. Because of the preceding Lemma the claim follows from the uniqueness of the fixed point of T. □ □

The following is indicated in [2, p. 4].

Theorem 2. *The energy functional $\mathcal{E}_{g,\alpha}$ is invariant under rotations of the density matrices, i.e., for all $\gamma\in F$ and all $R\in SO(3)$ we have*

$$\mathcal{E}_{g,\alpha}(\gamma) = \mathcal{E}_{g,\alpha}(\gamma_R).$$

Proof. We remark that $2E(\gamma,\gamma) = \operatorname{tr} X^{(\gamma)}\gamma$ and $2D(\rho_\gamma,\rho_\gamma) = \operatorname{tr}\phi^{(\gamma)}\gamma$. But for any $f \in H^1(\mathbb{R}^3)^4$, any $\gamma \in F$ and any $R \in SO(3)$ we get, using (3), (4), (5)(6), and (7),

$$(f_R, D_g f_R) = \int_G \overline{V_R f(Q\mathbf{x})}^t V_R(D_g f)(Q\mathbf{x})\mathrm{d}x = (f, D_g f) \tag{8}$$

$$(f_R, X^{(\gamma_R)} f_R) = \int_G \overline{V_R f(Q\mathbf{x})}^t V_R(X^{(\gamma)} f)(Q\mathbf{x})\mathrm{d}x = (f, X^{(\gamma)} f) \tag{9}$$

$$(f_R, \phi^{(\gamma_R)} f_R) = \int_G \overline{V_R f(Q\mathbf{x})}^t V_R(\phi^{(\gamma)} f)(Q\mathbf{x})\mathrm{d}x = (f, \phi^{(\gamma)} f) \tag{10}$$

This proves the claim. □ □

5. Solutions of the Dirac-Fock Equations Minimize the Energy of Electron-Positron Field

In this section we show that the solution of the Dirac-Fock equations, which we constructed above, yields a minimizer of the Dirac-Fock functional on the set of all density matrices, if the quantization is chosen with respect to this solution. To prove this, we need a technical remark:

Definition 2. *Let $\gamma \in F$ and P_- an orthogonal projector. γ is called density matrix with respect to P_-, if and only if the operator inequality*

$$0 \le \gamma + P_- \le 1$$

is fulfilled.

For density matrices with respect to P_- the following lemma is valid:

Lemma 5. *Let γ be a density matrix with respect to P_- and let $P_+ := 1 - P_-$. Then the following operator inequalities hold:*

$$P_-\gamma P_- P_-\gamma P_- + P_-\gamma P_+ P_+\gamma P_- \le -P_-\gamma P_-$$
$$P_+\gamma P_+ P_+\gamma P_+ + P_+\gamma P_- P_-\gamma P_+ \le P_+\gamma P_+.$$

Proof. The proof is a consequence of the fact that from $0 \le \gamma + P_- \le 1$ it follows that $(\gamma + P_-)^2 \le \gamma + P_-$ (see [1], Equations (18) and (19)). □ □

With these preparations the main result of this section is a corollary of the following theorem:

Theorem 3. *Assume $\delta = \chi_{[0,\epsilon_N^{(\delta)}]}(D_{g,\alpha}^{(\delta)})$ and $N = \operatorname{tr}\delta$. Let $\gamma \in \widetilde{\mathcal{S}}^{(\delta)}$, and $\gamma' := \gamma - \delta$ Moreover, assume $0 < \frac{\pi}{4} c_{g,\alpha,N}\alpha < 1$. Then*

$$\mathcal{E}_{g,\alpha}(\gamma) \ge \mathcal{E}_{g,\alpha}(\delta), \tag{11}$$

if one of the following conditions is fulfilled:

(1) *The density matrix γ' is an orthogonal perturbation of δ, i.e., $\delta\gamma'\delta = 0$.*
(2) *$\gamma \in \widetilde{\mathcal{S}}_{\partial N}^{(\delta)}$, and the difference $\epsilon_{N+1}^{(\delta)} - \epsilon_N^{(\delta)}$ is so big that*

$$(1 - \tfrac{\pi}{4} c_{g,\alpha,N}\alpha)\epsilon_{N+1}^{(\delta)} - (1 + \tfrac{\pi}{4} c_{g,\alpha,N}\alpha)\epsilon_N^{(\delta)} \ge 0. \tag{12}$$

Proof. First of all we note that the hypothesis implies $\epsilon_{N+1}^{(\delta)} > \epsilon_N^{(\delta)}$. We set $P_- := \chi_{(-\infty,\epsilon_N^{(\delta)}]}(D_{g,\alpha}^{(\delta)})$ and $P_+ := 1 - P_-$. This choice of the projectors means shifting the Dirac sea in such a way that the eigenfunctions of the occupied orbitals belong to the Dirac sea.

We now choose the density matrix $\gamma \in \widetilde{\mathcal{S}}^{(\delta)}$ arbitrarily. We have

$$0 \le \gamma + \Lambda_- = \gamma' + \delta + \Lambda_- = \gamma' + P_- \le 1,$$

i.e., γ' is a density matrix with respect to P_-, where $\Lambda_+ := \Lambda_+^{(\delta)}$ and $\Lambda_- := \Lambda_-^{(\delta)}$. We now plug γ into the functional and get

$$\begin{aligned}\mathcal{E}_{g,\alpha}(\gamma) &= \mathrm{tr}\left(D_g\left(\gamma'+\delta\right)\right)+\alpha Q\left(\gamma'+\delta,\gamma'+\delta\right)\\ &= \mathrm{tr}\left(D_g\delta\right)+\alpha Q\left(\delta,\delta\right)+\mathrm{tr}\left(D_g\gamma'\right)+2\alpha Q\left(\delta,\gamma'\right)+\alpha Q\left(\gamma',\gamma'\right)\\ &= \mathcal{E}_{g,\alpha}\left(\delta\right)+\mathrm{tr}\,D_{g,\alpha}^{(\delta)}\gamma'+\alpha Q\left(\gamma',\gamma'\right)\geq \mathcal{E}_{g,\alpha}\left(\delta\right)+\mathrm{tr}\,D_{g,\alpha}^{(\delta)}\gamma'-\alpha E(\gamma',\gamma').\end{aligned}$$

Moreover,

$$\begin{aligned}\gamma'\gamma' = {}& P_+\gamma'P_+\gamma'P_+ + P_+\gamma'P_+\gamma'P_- + P_+\gamma'P_-\gamma'P_+ + P_+\gamma'P_-\gamma'P_-\\ &+ P_-\gamma'P_-\gamma'P_- + P_-\gamma'P_-\gamma'P_+ + P_-\gamma'P_+\gamma'P_- + P_-\gamma'P_+\gamma'P_+.\end{aligned}$$

Using Lemma 10 and Lemma 12 we calculate $E(\gamma',\gamma')$ because of the inequalities of Lemma 5. Also all terms of the form

$$\mathrm{tr}(|D_{g,\alpha}^{(\delta)}|^{\frac12}P_-\gamma'P_+P_+\gamma'P_+|D_{g,\alpha}^{(\delta)}|^{\frac12})$$

vanish, since the spectral projectors commute with $D_{g,\alpha}^{(\delta)}$.

$$\begin{aligned}E(\gamma',\gamma') &\leq \tfrac{\pi}{4}\,\mathrm{tr}\left(\gamma'|\nabla|\gamma'\right)\leq \tfrac{\pi}{4}c_{g,\alpha,N}\,\mathrm{tr}(\gamma'\left|D_{g,\alpha}^{(\delta)}\right|\gamma')\\ &\leq \tfrac{\pi}{4}c_{g,\alpha,N}\,\mathrm{tr}\left(|D_{g,\alpha}^{(\delta)}|^{\frac12}(P_+\gamma'P_+-P_-\gamma'P_-)||D_{g,\alpha}^{(\delta)}|^{\frac12}\right)\\ &= \tfrac{\pi}{4}c_{g,\alpha,N}\,\mathrm{tr}\left(D_{g,\alpha}^{(\delta)}(P_+\gamma'P_++\Lambda_-\gamma'\Lambda_--\delta\gamma'\delta)\right)\end{aligned}$$

Moreover,

$$\mathrm{tr}\,D_{g,\alpha}^{(\delta)}\gamma' = \mathrm{tr}\left(D_{g,\alpha}^{(\delta)}(P_+\gamma'P_++\Lambda_-\gamma'\Lambda_-+\delta\gamma'\delta\right),$$

i.e., we get altogether

$$\begin{aligned}\mathcal{E}_{g,\alpha}(\gamma) &= \mathcal{E}_{g,\alpha}\left(\delta\right)+\mathrm{tr}\,D_{g,\alpha}^{(\delta)}\gamma'+\alpha Q(\gamma',\gamma')\\ &\geq \mathcal{E}_{g,\alpha}\left(\delta\right)+\left(1-\tfrac{\pi}{4}c_{g,\alpha,N}\alpha\right)\mathrm{tr}\,D_{g,\alpha}^{(\delta)}P_+\gamma'P_+\\ &\quad+\left(1+\tfrac{\pi}{4}c_{g,\alpha,N}\alpha\right)\mathrm{tr}\,D_{g,\alpha}^{(\delta)}\delta\gamma'\delta+\left(1-\tfrac{\pi}{4}c_{g,\alpha,N}\alpha\right)\mathrm{tr}\,D_{g,\alpha}^{(\delta)}\Lambda_-\gamma'\Lambda_-.\end{aligned}$$

We see that the energy grows, if γ' is an orthogonal perturbation of δ, because in this case $\delta\gamma'\delta=\delta(\gamma-\delta)\delta=0$. This shows the first part of the claim.

We prove now the second claim: from now assume $\gamma\in\widetilde{\mathcal{S}}_{\partial N}^{(\delta)}$. Since $\mathrm{tr}\,\gamma=\mathrm{tr}\,\delta$, we have $\mathrm{tr}\,\gamma'=0$. Moreover,

$$\mathrm{tr}\,\gamma'=\mathrm{tr}\,\Lambda_-\gamma'\Lambda_-+\mathrm{tr}\,\delta\gamma'\delta+\mathrm{tr}\,P_+\gamma'P_+,$$

such that

$$0\leq -\mathrm{tr}\,\Lambda_-\gamma'\Lambda_-=\mathrm{tr}\,\delta\gamma'\delta+\mathrm{tr}\,P_+\gamma'P_+,$$

because $\Lambda_-\gamma'\Lambda_-=\Lambda_-\gamma\Lambda_-$ is a negative operator. It follows

$$\mathrm{tr}\,\delta\gamma'\delta\geq -\mathrm{tr}\,P_+\gamma'P_+.$$

Note that $\mathrm{tr}\,\delta\gamma'\delta\leq 0$ holds. We even have $-1\leq\delta\gamma'\delta\leq 0$, since

$$\begin{aligned}(f,\delta\gamma'\delta f) &= (f_{DF},\delta\gamma'\delta f_{DF})\\ &= (f_{DF},\delta\gamma\delta f_{DF})-(f_{DF},\delta f_{DF})\leq (f_{DF},\Lambda_+f_{DF})-(f_{DF},f_{DF})=0\end{aligned}$$

and

$$\begin{aligned}(f,\delta\gamma'\delta f) &= (f_{DF},\delta\gamma'\delta f_{DF})=(f_{DF},\delta\gamma\delta f_{DF})-(f_{DF},\delta f_{DF})\\ &\geq -(f_{DF},\Lambda_-f_{DF})-(f_{DF},f_{DF})=-(f_{DF},f_{DF})\geq -(f,f),\end{aligned}$$

where we set $f_{DF}:=\delta f$.

Let now λ_i, $i = 1, \ldots, N$, and f_i, $i = 1, \ldots, N$, eigenvalues and the corresponding eigenvectors of $\delta\gamma'\delta$, and $\lambda_i, i > N$, and $f_i, i > N$, eigenvalues and corresponding eigenvectors of $P_+\gamma' P_+$. Then

$$\operatorname{tr} D^{(\delta)}_{g,\alpha}\delta\gamma'\delta = \sum_{i=1}^{N} \lambda_i \left(f_i, D^{(\delta)}_{g,\alpha} f_i\right) \geq \epsilon^{(\delta)}_N \operatorname{tr} \delta\gamma'\delta \geq -\epsilon^{(\delta)}_N \operatorname{tr} P_+\gamma' P_+$$

and

$$\operatorname{tr} D^{(\delta)}_{g,\alpha} P_+\gamma' P_+ = \sum_{i=N+1}^{\infty} \lambda_i \left(f_i, D^{(\delta)}_{g,\alpha} f_i\right) \geq \epsilon^{(\delta)}_{N+1} \operatorname{tr} P_+\gamma' P_+$$

hold. It follows that

$$\begin{aligned}(13)\quad \mathcal{E}_{g,\alpha}(\gamma) - \mathcal{E}_{g,\alpha}(\delta) &\geq (1 - \tfrac{\pi}{4} c_{g,\alpha,N}\alpha) \operatorname{tr} D^{(\delta)}_{g,\alpha} P_+\gamma' P_+ \\ &\quad + (1 + \tfrac{\pi}{4} c_{g,\alpha,N}\alpha) \operatorname{tr} D^{(\delta)}_{g,\alpha} \delta\gamma'\delta \\ &\geq (1 - \tfrac{\pi}{4} c_{g,\alpha,N}\alpha)\epsilon^{(\delta)}_{N+1} \operatorname{tr} P_+\gamma' P_+ - (1 + \tfrac{\pi}{4} c_{g,\alpha,N}\alpha)\epsilon^{(\delta)}_N \operatorname{tr} P_+\gamma' P_+ \\ &= [(1 - \tfrac{\pi}{4} c_{g,\alpha,N}\alpha)\epsilon^{(\delta)}_{N+1} - (1 + \tfrac{\pi}{4} c_{g,\alpha,N}\alpha)\epsilon^{(\delta)}_N] \operatorname{tr} P_+\gamma' P_+\end{aligned}$$

Since $\operatorname{tr} P_+\gamma' P_+ = \operatorname{tr} P_+\gamma P_+ \geq 0$, this shows the claim. □ □

Setting $a := (2\pi N^2 - 1/8\pi^2 N)\epsilon^0_N$, $b := ((4N - 1/4\pi - 1/2\pi N)\epsilon^0_N - (4N + 1/4\pi)\epsilon^0_{N+1})\, b_g$ and $c := (\epsilon^0_{N+1} - \epsilon^0_N)(b_g)^2$ we define

$$k_{g,N} := (-b - \sqrt{b^2 - 4ac})(2a)^{-1}.$$

Corollary 4. *Assume $N \in CS$, δ as in Theorem 3, and $\alpha \leq \min\{k_{g,N}, \frac{b_g}{4N}\}$. Then*

$$(14)\qquad \mathcal{E}_{g,\alpha}(\delta) = E^{DF}_N := \inf\{\mathcal{E}_{g,\alpha}(\gamma) | \gamma \in \widetilde{\mathcal{S}}^{(\delta)}_{\partial N}\}.$$

Proof. It suffices to verify (12) of Theorem 3. By Lemma 2 it suffices to show

$$\left(1 - \tfrac{\pi}{4} c_{g,\alpha,N}\alpha\right) \epsilon^0_{N+1} - \left(1 + \tfrac{\pi}{4} c_{g,\alpha,N}\alpha\right) \cdot (1 + \tfrac{\pi}{2}\alpha N b_g^{-1})\epsilon^0_N \geq 0$$

in order to fulfill inequality (12) of Theorem 3. This condition leads to the quadratic equation

$$\begin{aligned}\left(2\pi N^2 - \tfrac{1}{8}\pi^2 N\right) \epsilon^0_N \alpha^2 + \left(\left(4N - \tfrac{1}{4}\pi - \tfrac{1}{2}\pi N\right) \epsilon^0_N - \left(4N + \tfrac{1}{4}\pi\right) \epsilon^0_{N+1}\right) b_g \alpha \\ + \left(\epsilon^0_{N+1} - \epsilon^0_N\right) (b_g)^2 = 0\end{aligned}$$

whose relevant smaller solution is given by $k_{g,N}$. □ □

We close with some remarks:

(1) In the spirit of Mittleman the ground state energy E^M_N of N relativistic electrons in the field of a nucleus with coupling constant g in Hartree-Fock approximation is defined as

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$$(15)\qquad E^M_N = \sup\{\inf\{\mathcal{E}_{g,\alpha}(\gamma) | \gamma \in \widetilde{\mathcal{S}}^{(\delta)}_{\partial N}\} | \delta \in F,\ \delta = \delta^2,\ \operatorname{tr}\delta = N\}.$$

Corollary 4 together with Equation (11) shows – under the hypotheses made there – that $E^M_N \geq E^{DF}_N$. The reverse inequality is valid – without restriction to closed shells – for α small enough (Barbaroux et al. [2, Formula (13)]), thus confirming that these different definitions of the ground state energies for closed shell atoms agree in the non-relativistic limit. In fact this shows even the BES conjecture in this case. (See Barbaroux et al. [2, Theorem 5]).

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(2) Since the BES conjecture is false in the open shell case [2, 4], the previous remark shows also that the restriction to the closed shell case is not of mere technical nature.

(3) Under the assumption that δ has a spherically symmetric density ρ_δ, one can show the assertion of Corollary 4 even for bigger α, using Lemma 3 instead of Lemma 2. The results of this (numerical) computation are shown additionally in Figure 3.

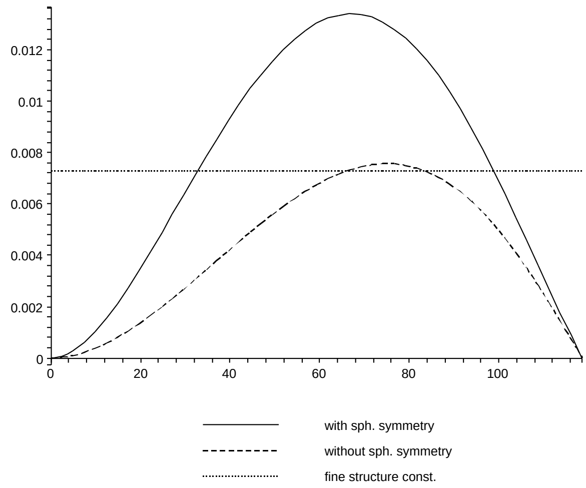

FIGURE 3. The maximal value of α for which we can guarantee that a projection $\delta \in DF$ onto the lowest eigenvalues of $D^{(\delta)}$ minimizes the energy in dependence on the nuclear charge $Z = 137g$ and $N = 2$.

APPENDIX A. THE MINIMAX PRINCIPLE OF GRIESEMER AND SIEDENTOP

In [8] the following minimax principle for eigenvalues of self-adjoint operators in spectral gaps was proven:

Theorem 4. *Suppose that A is a self-adjoint operator in a Hilbert space $\mathfrak{h} = \mathfrak{h}_+ \oplus \mathfrak{h}_-$ where $\mathfrak{h}_+ \perp \mathfrak{h}_-$. Let $\Lambda_\pm$ be the orthogonal projectors onto $\mathfrak{h}_\pm$ and let $\mathfrak{Q}$ be a subspace with $\mathcal{D}(A) \subset \mathfrak{Q} \subset \mathcal{Q}(A)$ and $\Lambda_\pm \mathfrak{h} \subset \mathfrak{Q}$, where $\mathcal{D}(A)$ and $\mathcal{Q}(A)$ denote operator domain and form domain of A respectively. Let $P_+ := \chi_{(0,\infty)}(A)$, $P_- := \chi_{(-\infty,0)}(A)$, $\mathfrak{Q}_\pm := \mathfrak{Q} \cap \mathfrak{h}_\pm$, and*

$$\lambda_n(A) := \inf_{\substack{M_+ \subset \mathfrak{Q}_+ \\ \dim(M_+)=n}} \sup_{\substack{\phi \in M_+ \oplus \mathfrak{Q}_- \\ \|\phi\|=1}} (\phi, A\phi).$$

(1) *If $(\phi, A\phi) \le 0$ for all $\phi \in \mathfrak{Q}_-$, then*

$$\lambda_n(A) \le \mu_n(A|P_+\mathfrak{h})$$

(2) *If $(\phi, A\phi) > 0$ for all non-vanishing $\phi \in \mathcal{Q}(A) \cap \mathfrak{h}_+$ and $(|A|+1)^{\frac{1}{2}} P_- \Lambda_+$ is bounded, then*

$$\lambda_n(A) \ge \mu_n(A|P_+\mathfrak{h}).$$

Here the μ_n denote the standard (Courant) minimax values of an operator bounded from below.

Appendix B. Properties of Dirac-Fock Operators

We list some useful inequalities from [1] and [3] and some slight improvements of these.

Lemma 6. *For any $\gamma \in F$ we have*

$$\phi^{(\gamma)} \leq \tfrac{\pi}{2}\||\nabla|\gamma\|_1 \leq \tfrac{\pi}{2}\||D_0|\gamma\|_1 = \tfrac{\pi}{2}\|\gamma\|_F, \tag{16}$$

$$\phi^{(\gamma)} \leq \tfrac{\pi}{2}\|\gamma\|_1|\nabla| \leq \tfrac{\pi}{2}\|\gamma\|_1|D_0|. \tag{17}$$

Lemma 7. *If $\gamma \in F$, then*

$$X^{(\gamma)} \leq \phi^{(|\gamma|)},\ \|X^{(\gamma)}\| \leq \|\phi^{(|\gamma|)}\|,\ \textit{and}\ \|W^{(\gamma)}\| \leq \|\phi^{(|\gamma|)}\|.$$

Proof. We prove only the third statement. Let $\gamma = \gamma_+ - \gamma_-$, i.e., γ_+ and γ_- are the positive and negative parts of γ respectively. Then

$$W^{(\gamma)} = \phi^{(\gamma_+)} - \phi^{(\gamma_-)} - X^{(\gamma_+)} + X^{(\gamma_-)} \leq \phi^{(\gamma_+)} + X^{(\gamma_-)} \leq \phi^{(\gamma_+)} + \phi^{(\gamma_-)} = \phi^{(|\gamma|)},$$

where we used Lemmata 8 and 7. In the same way we get $W^{(\gamma)} \geq -\phi^{(\gamma_-)} - X^{(\gamma_+)} \geq -\phi^{(\gamma_-)} - \phi^{(\gamma_+)} = -\phi^{(|\gamma|)}$, so $|(f, W^{(\gamma)}f) \leq (f, \phi^{(|\gamma|)}f)$ for all $f \in \mathfrak{H}$. This immediately implies the claim. □ □

Lemma 8. *Let $0 \leq \gamma \in F$, then $0 \leq X^{(\gamma)} \leq \phi^{(\gamma)}$; in particular $0 \leq W^{(\gamma)}$.*

An immediate consequence of the preceding lemmata is

Lemma 9. *If $\gamma = \gamma^* \in \mathfrak{S}^1(\mathfrak{H})$ and $\gamma' \in F$, then*

$$\begin{aligned} |D(\rho_\gamma, \rho_{\gamma'})| &\leq \tfrac{\pi}{4}\|\gamma\|_1 \operatorname{tr}(|\nabla||\gamma|), \\ E(\gamma, \gamma') &\leq D(\rho_{|\gamma|}, \rho_{|\gamma'|}). \end{aligned}$$

We also need

Lemma 10 (Bach et al. [1])**.** *For all $\gamma \in F$ we have $E(\gamma, \gamma) \leq \frac{\pi}{4} \operatorname{tr}(\gamma|\nabla|\gamma)$.*

Lemma 11. *Pick $\gamma \in F$, $g \in (-\sqrt{3}/2, \sqrt{3}/2)$, $\alpha \in \mathbb{R}$. $W^{(\gamma)}$ is relatively compact with respect to D_0. The operator $D_{g,\alpha}^{(\gamma)}$ is self-adjoint with $\mathcal{D}(D_{g,\alpha}^{(\gamma)}) = \mathcal{D}(D_g) = H^1(\mathbb{R}^3)^4$ and*

$$\sigma_{\mathrm{ess}}(D_{g,\alpha}^{(\gamma)}) = \sigma_{\mathrm{ess}}(D_g) = (-\infty, -1] \cup [1, \infty).$$

Lemma 12. (1) *Set $C_g := (\sqrt{4g^2+9} - 4g)/3$ and, for $0 \leq g < \sqrt{3}/2$,*

$$d_g := (1 + C_g^2 - \sqrt{(1 - C_g^2)^2 + 4g^2 C_g^2})/2.$$

Then, we for $g \in [0, \sqrt{3}/2]$ according to Morozov ([10])

$$|D_g|^2 \geq d_g^2 |D_0|^2.$$

If we assume in addition $\gamma \in F$ and $d_g - 4|\alpha|\|\gamma\|_1 > 0$, then

$$|D_{g,\alpha}^{(\gamma)}|^2 \geq (d_g - 4|\alpha|\|\gamma\|_1)^2 |D_0|^2$$

(2) *Setting $b_g := \sqrt{1-g^2}(\sqrt{4g^2+9} - 4g)/3$ and $g \in (0, \sqrt{3}/2)$ we have*

$$|D_g|^2 \geq b_g^2 |\nabla|^2.$$

Assuming in addition $b_g - 4|\alpha|\|\gamma\|_1 > 0$ implies the inequalities

$$\begin{aligned} |D_{g,\alpha}^{(\gamma)}|^2 &\geq (b_g - 4|\alpha|\|\gamma\|_1)^2 |\nabla|^2, \\ |D_{g,\alpha}^{(\gamma)}|^2 &\geq (1 - 4|\alpha|\|\gamma\|_1 b_g^{-1})^2 |D_g|^2. \end{aligned}$$

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